

## **Photostability of Liquid Mixture Based on Rhodamine 590 Dye in Vinyl Acetate Polymer Solution**

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### **Abstract**

The photostability of Rhodamine 590 perchlorate laser dye in various concentration mixture ratios of Rhodamine 590 perchlorate and Vinyl acetate polymer solutions has been measured to determine the longevity of laser operation when pumped by the second harmonic of a Q-switched Nd:YAG laser. Vinyl acetate polymer solution was prepared in methanol and was used as triplet quencher additive to improve efficiency and photostability performance. Higher efficiency and photostability were obtained at low ratio of Vinyl acetate polymer solution used as additive compared with pure dye. Maximum efficiency of 45 % with photostability of 165 GJ/mol was recorded and discussed. This paper identifies new additive material that could be used for improving photostability and efficiency of Rhodamine dye.

### **Introduction**

The photostability of laser dyes is a very important subject because the photostability of liquid and solid dye lasers is relatively low after long operation of dye laser [1-2]. This reduction in lasing ability is due to the formation of a large number of triplet states with longer lifetime than the singlet states contributing to the laser action. The longer triplet lifetime will affect the laser performance in both reduced photostability and efficiency of the laser output. Many attempts have been made to decrease the triplet states concentration in both liquid and solid state dye laser by addition of

various types of additive triplet quenchers such as 2,2,6,6 Tetramethylpiperdin (TMP)[3], Tinuvin 770[4], Triphenylamine[5], 1,4-Diazobicyclo [2,2,2] Octane (DABCO)[6], and 1,3,5,7-Cyclooctatetraene (COT)[7].

In this work Vinyl acetate polymer solution was prepared in Methanol solvent. This solution was used as triplet quencher additive to improve efficiency and photostability performance. Vinyl acetate monomer is colorless liquid which has varied industrial application such as paint, paper coatings, aerosol hair sprays and shampoos [8]. Linear and nonlinear optical properties of vinyl acetate monomer solution such as molar electronic polarizability, contraction, mean polarizability, radius of molecule and optical polarizability, describing the temperature dependence of the refractivity for Vinyl acetate monomer were calculated recently[9]. All related microscopic parameters concerning the molecular structure such as nonlinear Kerr constants, anisotropic factors, optical anisotropy and orientation function was also calculated [9].

There are many reasons for low photostability of dye and degradation of the dye molecule after some time of using. These reasons are: (i) photo deactivation from the excited state caused by chemical oxidation reaction; (ii) formation of dimmers that absorb irradiation without any fluorescence; (iii) thermal destruction. Therefore there is a need to use a different type of additive to improve the photostability and efficiency of dye and minimize the reaction that causes degradation of dyes. This paper identifies new additive material that could be used for improving photostability and efficiency of Rhodamine dye.

## **Experimental**

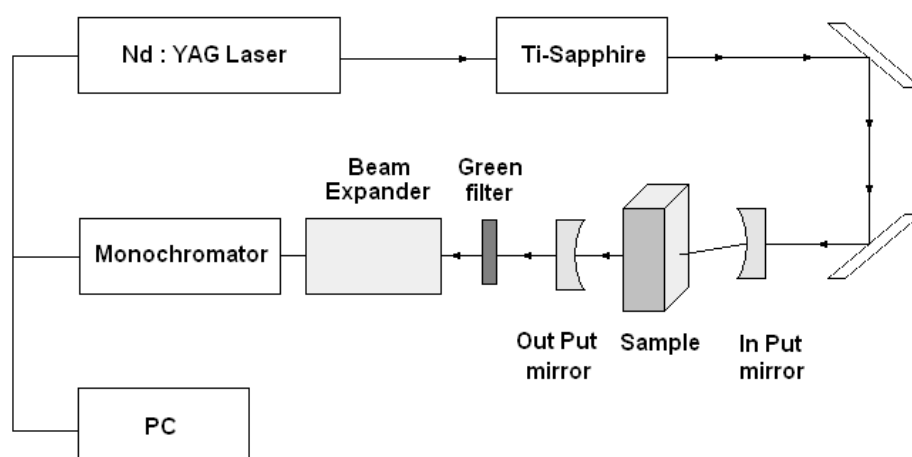
Preparation of Vinyl acetate polymer and Rhodamine 590 perchlorate:

Vinyl acetate polymer was prepared by using a redox initiator [8]. A mixture of 0.005g Ferrous sulfate heptahydrate, 0.01g Sodium persulfate, and 0.01g Sodium metabisulfite from Aldrich was used as a redox initiator without further purification to polymerize Vinyl acetate monomer. Vinyl acetate monomer from Aldrich was purified with three washes with 10% Sodium bicarbonate, followed by three washes with distilled water to remove the hydroquinone inhibitor and dried with anhydrous Sodium sulfate, and the material was then refrigerated at 10 °C until use. Mixture of redox initiator was added to 5ml of Vinyl acetate monomer and 50 ml of Methanol solvent and stirred at room temperature to form vinyl acetate polymer solution. Rhodamine 590 perchlorate from Exciton was prepared in methanol solvent with different concentrations.

## **Experimental Set Up**

The photostability was studied by using the experimental set up[10] as shown in Fig (1). The pump source was a Q-switched Nd:YAG laser operating at the second harmonic of 532 nm. The pump delivered up to 60 mJ/pulse in 10 ns at 1-10 Hz repetition rate or in a single pulse. The input mirror was dichroic with 90% transmission at 532 nm and 95% reflectivity at 575 nm. The output mirror was 70%

reflection at 532 nm and 30% transmission at 575 nm. The length of cavity was 15 mm to reduce the cavity losses due to a highly divergent output. The pump beam has diameter of 2.0 mm and was aligned off-axis from the sample cell at a slight tilt angle of  $16^\circ$  to the resonator axis so that any transmitted green pump light was not collinear with the output beam and was not incident on the volume absorbing power meter [10]. The photostability measurements on samples were performed at  $0.16 \text{ J/cm}^2$  and at 10 Hz repetition rate. The laser performance of solution sample was evaluated using 3 ml of total volume of dye solution and poly vinyl acetate solution in methanol with a range of dye concentrations ( $1 \times 10^{-3} \text{ M}$ ,  $1 \times 10^{-4} \text{ M}$  and  $1 \times 10^{-5} \text{ M}$ ) in a 10 mm optical path length silica cuvette. The data retrieved and analyzed using Picolog software model ACD-12 from Picolog Technology Company, UK.



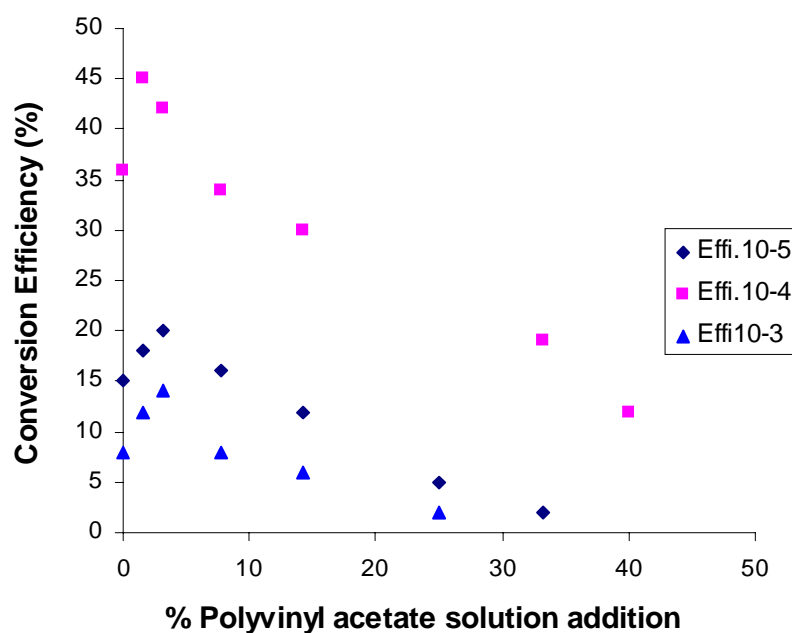
**Figure 1:** Experimental set up of dye laser

## Results and Discussion

In previous studies, fluorescence and laser performance had been observed in Rhodamine 590 dye [11, 12]. However, the introduction of additives may lead to changes in fluorescence and laser performance. Many photochemical studies have been focused on Rhodamine 590 which have been deployed with both steady-state and pulse photolysis techniques. Weber presented [13] evidence that triplet quenchers, oxygen and 1,3,5,7-Cyclooctatetraene, COT, were included, which slowed decomposition rate R590. Britt and Moniz [14] reported that addition of acid or base has a moderate effect on quantum yield of R590 bleaching on 514 nm irradiation in ethanol.

In this work, the photostability of Rhodamine 590 perchlorate was enhanced using vinyl acetate polymer solution as a triplet quencher additive. The efficiencies of different Rhodamine 590 perchlorate dye concentrations ( $1 \times 10^{-3} \text{ M}$ ,  $1 \times 10^{-4} \text{ M}$  and  $1 \times 10^{-5} \text{ M}$ ) with the presence of various content of Vinyl acetate polymer as an additive

are shown in Fig (2). It is seen that upon using low percentage of 1.6 and 3.2 % polymer solution as additive for Rhodamine 590 perchlorate of varying concentrations, the mixture shows higher efficiency and photostability compared with only pure Rhodamine 590 perchlorate. It is noticed that the increase of efficiency from 36 % for pure dye to 45 % when using 1.6 % of poly vinyl acetate as additive as shown in Table1.

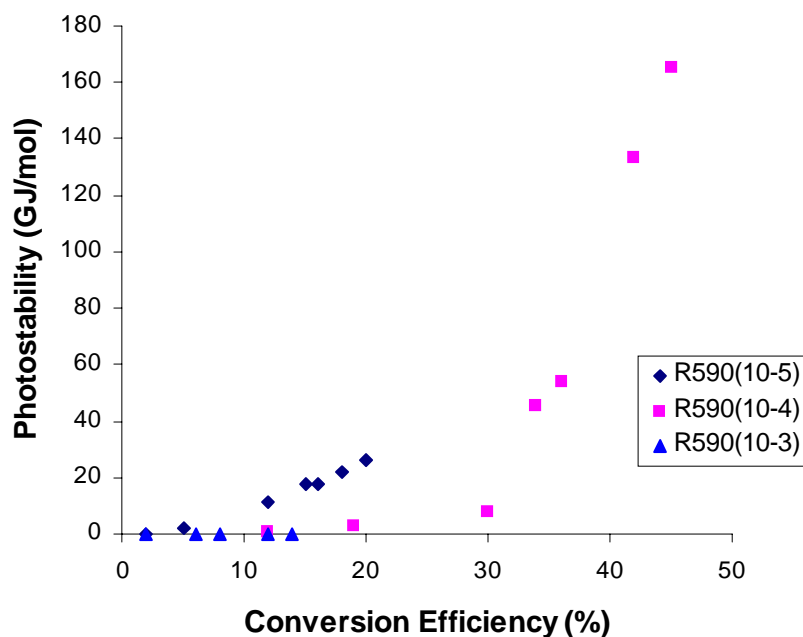


**Figure 2:** Efficiency of Rodamine 590 at different percentage of Vinyl acetate polymer solution addition.

The concentration of Rhodamine 590 perchlorate was found ( $1 \times 10^{-4}$  M) to be the optimum in terms of efficiency (45 %) and photostability (165 GJ/mol) with 1100000 numbers of pulses shots as shown in Fig.(3) and Table1. These improvements in lasing behavior could be ascribed to the reduction of the number of long lifetime triplet states in comparison to singlet states which contribute to the laser action. The longer life time of triplet states is known to reduce photostability and efficiency.

The ability of Vinyl acetate polymer solution to decline the lifetime of triplet states in improving the efficiency and photostability when using 1.6 and 3.2 % polymer solutions might be attributed to the better dispersion of the dye by the polymer chain (Tables 1, 2, 3). Concentration of dye is a very important factor to determine the photostability of dye. Higher concentration of dye such as  $10^{-3}$  M will lead to aggregation of dye molecules [11] to form dimmers thereby reducing the photostability as compared to  $10^{-4}$  M concentration, shown in Table 1 and 3. The structure of Rhodamine 590 is very important to improve the photostability and efficiency. Rhodamine 590 perchlorate as shown in Fig (4) shows larger quantum yield

and larger conversion efficiency compared with Rhodamine 590 chloride [15]. This conversion efficiency can be improved by adding additive such as ethyl alcohol-carbonic acid ether mixture [15].



**Figure 3:** Conversion efficiency vs. photostability of Rodamine 590 perchlorate.

**Table 1:** Performance of Rodamine 590 perchlorate ( $1 \times 10^{-4}$  M) Laser Dye in Various Vinyl acetate Polymer Solution Additives.

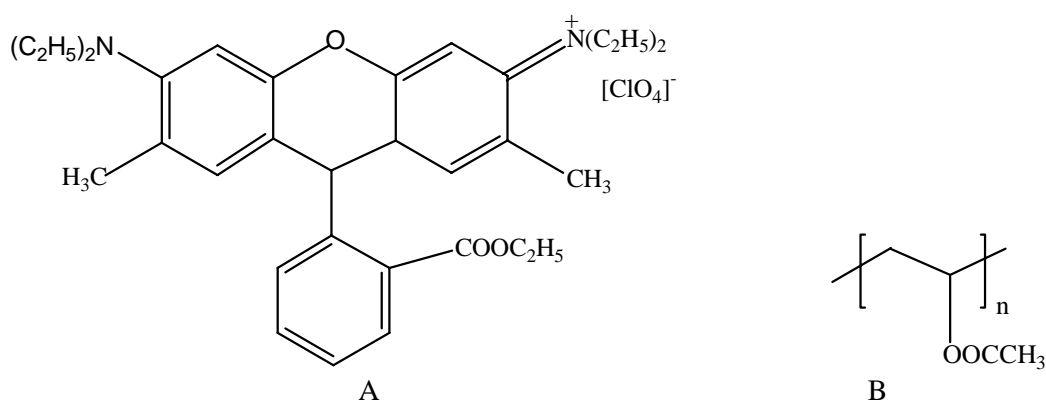
% Polymer Solution	% Conversion Efficiency	Number of Pulses to 50% Reduction	Photostability (GJ/mol)
0.0	36	450,000	54
1.6	45	1,100,000	165
3.2	42	950,000	133
7.7	34	389,600	45
14.2	30	80,000	8.0
33.3	19	45,000	3.0
40	12	27,000	1.0

**Table 2:** Performance of Rhodamine 590 perchlorate ( $1 \times 10^{-5}$  M) Laser Dye in Various Vinyl acetate Polymer Solution Additives.

% Polymer Solution	% Conversion Efficiency	Number of Pulses to 50% Reduction	Photostability (GJ/mol)
0.0	15	35000	18
1.6	18	36860	22
3.2	20	38600	26
7.7	16	34500	18
14.2	12	28350	11
25	5	12700	2.0
33.3	2	4680	0.3

**Table 3:** Performance of Rhodamine 590 perchlorate ( $1 \times 10^{-3}$  M) Laser Dye in Various Vinyl acetate Polymer Solution Additives.

% Polymer Solution	% Conversion Efficiency	Number of Pulses to 50% Reduction	Photostability (GJ/mol)
0.0	8	11800	0.03
1.6	12	15200	0.06
3.2	14	18500	0.08
7.7	8	10600	0.03
14.2	6	8800	0.02
25	2	4900	0.004

**Figure 4:** Structure of Rhodamine 590 perchlorate (A), Vinyl acetate polymer (B)

## Conclusions

The effect of addition of small quantity of Vinyl acetate polymer solution on photostability of Rhodamine 590 perchlorate dyes has been investigated. Vinyl acetate polymer solution was used as triplet quencher additive to improve efficiency and photostability performance. Higher efficiency and photostability were obtained compared to pure dye at low ratio of Vinyl acetate polymer solution used as triplet quencher additive. Maximum efficiency of 45 % with photostability of 165 GJ/mol was observed. This paper identifies new additive material that could be used for improving photostability and efficiency of Rhodamine dye.

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